COORDINATION COMPOUNDS OF ELEMENTS OF THE IB FAMILY

BY

BURTON PETER BLOCK

B.S., Harvard University, 1944
M.S., University of Tennessee, 1945

AN ABSTRACT OF A THESIS

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN CHEMISTRY
IN THE GRADUATE COLLEGE OF THE
UNIVERSITY OF ILLINOIS, 1949

URBANA, ILLINOIS

1949

COORDINATION COMPOUNDS OF ELEMENTS OF THE IB FAMILY

BY

BURTON PETER BLOCK

B.S., Harvard University, 1944
M.S., University of Tennessee, 1945

AN ABSTRACT OF A THESIS

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN CHEMISTRY
IN THE GRADUATE COLLEGE OF THE
UNIVERSITY OF ILLINOIS, 1949

URBANA, ILLINOIS

1949

ACKNOWLEDGMENT

The author would like to take this opportunity to express his deepest gratitude to those who have assisted him in the execution of this study. He is most indebted to Dr. John C. Bailar, Jr., for assuming the guidance of his research when he was forced to leave Purdue University because of circumstances beyond his control. He is also extremely grateful to Doctors D. W. Pearce and W. C. Fernelius for their counsel in the early stages of the problem at Purdue.

For assistance with various parts of the experimental and theoretical work, he would like to thank several members of the staff, and several of his fellow students in the Graduate School. Individual acknowledgments will be found in the portions of the thesis concerned.

Last, but no means least, he would like to express his appreciation for the understanding which his wife, Viola, has maintained throughout his graduate study and to thank her for her assistance in the preparation of this manuscript.

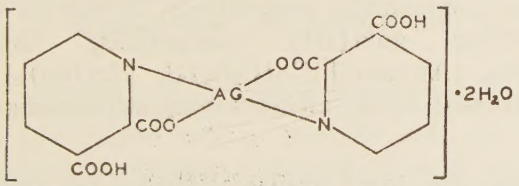
R. UNIV.
BIBLIOTHEEK
LEIDEN

COORDINATION COMPOUNDS OF ELEMENTS OF THE IB FAMILY

A. Silver compounds

Nakatsuka has reported that silver acetate reacts with 8-quinolinol to form bis(8-quinolinolo)silver(II) and metallic silver (5). Since silver(II) is a powerful oxidizing agent and 8-quinolinol is oxidized rather readily, it is doubtful if a compound such as the one described by Nakatsuka can exist. His work has been repeated and the supposed silver(II) compound investigated. Magnetic evidence and bromine titrations indicate that it is really a silver(I) complex of 8-quinolinol. It appears that Nakatsuka was effecting the same change from a yellow silver(I) compound to a green silver(I) compound which Hein and Regler brought about by recrystallizing the former compound from concentrated ammonia (4). The metallic silver formed is probably due to some reduction of silver acetate by 8-quinolinol at the higher temperature used in the preparation of the green compound.

A magnetic measurement showed that bis(quinolinato)-silver(II) contained one unpaired electron, as expected for bivalent silver, thus confirming Burada's findings (1). It is proposed that the structure of this compound is



B. o-Phenanthroline and α,α'-dipyridyl complexes of gold

Chloroauric acid forms two compounds with o-phenanthroline which were found to be $[Au(o\text{-phen})Cl_2]Cl$ and $[Au(o\text{-phen})Cl_2][AuCl_4]$. The proof of the structure for the former is based on its solubility in water and the products it

forms in metathetical reactions, while the structure given for the latter is shown to be highly probable from consideration of both the method of preparation and of the unfavorable steric relationships in the bridged structure which might be an alternate proposal. α,α'-Dipyridyl forms a compound which is very similar to the latter o-phenanthroline complex, and so is probably $[Au(dipy)Cl_2][AuCl_4]$. There is evidence that another compound, $[Au(dipy)Cl_2]Cl$, can be formed under the proper conditions, but it reverts very readily to the aforementioned complex. Other gold complexes prepared with these two coordinating agents are $[Au(o\text{-}phen)Br_2]Br$ and $[Au(dipy)Br_2][AuBr_4]$.

C. Ethylenediamine complexes of gold

The complex ion which is formed by gold(III) and ethylenediamine is dependent upon the pH of the solution. In slightly acidic solutions $[Au(en)_2]^{+3}$ is formed, while $[Au(en)(en\text{-}H)]^{+2}$ is formed in basic solutions. The former cation has been reported previously by Gibson and Colles (3) in the compound $[Au(en)_2]Br_3$, but in following their procedure the author always found $[Au(en)(en\text{-}H)]Br_2$ to be the product, so their directions are not adequate. The proof of structure is based on polarographic reductions and pH titrations, the former showing that the gold is tervalent in both compounds and the latter showing that acids and bases react with the two compounds, respectively, in one to one ratios. The following gold(III) compounds, $[Au(en)_2]Cl_3$, $[Au(en)_2]Br_3$, $[Au(en)_2][Co(C_2O_4)_3]$, $[Au(en)_2](picrate)_3$, and $[Au(en)(en\text{-}H)]Br_2$, all containing ethylenediamine, were prepared.

Qualitative structural studies confirmed the above analysis in so far as infrared spectra showed that $[Au(en)_2]Br_3$ is more symmetrical than $[Au(en)(en\text{-}H)]Br_2$, and x-ray studies showed that $[Pd(en)_2]Br_2$ and $[Au(en)(en\text{-}H)]Br_2$ have very similar crystal structures.

By titrating solutions of potassium bromoaurate directly

with dilute solutions of ethylenediamine and propylenediamine and following the variations in pH, it was found that the two diamines behave similarly. Initially there is a decrease in pH with formation of a precipitate; so the first reaction is postulated to be $[AuBr_4]^- +$ diamine $\rightarrow$ $[Au(\text{diamine-H})Br_2] + 2Br^- + H^+$. As more diamine is added, further hydrogen ions are apparently not lost, and at the first break, which corresponds to the addition of one mole of diamine per mole of gold, most of the gold is probably present as $[Au(\text{diamine})Br_2]^+$. When two equivalents of diamine have been added, the main species present is $[Au(\text{diamine})_2]^{+3}$, while when three equivalents of diamine have been added $[Au(\text{diamine})(\text{diamine-H})]^{+2}$ predominates. The similarity in the curves indicates that propylenediamine loses a hydrogen at higher pH values in the same way ethylenediamine does.

From the titration of $[Au(en)(en\text{-}H)]^{+2}$ with sodium hydroxide it appears that another hydrogen ion may be lost at a still higher pH to give $[Au(en\text{-}H)_2]^+$.

D. Attempted preparation of gold phthalocyanine

During the investigation of gold phthalocyanines a synthesis for phthalonitrile was evolved from reactions in the literature. Phthalic anhydride is converted to phthalimide (6), which is in turn converted to phthalamide (2) by reactions with ammonia. Phthalonitrile is prepared by the dehydration of phthalamide with phosphorus(V) oxychloride (7).

Reactions were carried out in which phthalonitrile was fused with chloroauric acid or metallic gold, phthalocyanine was refluxed with solutions of chloroauric acid in high boiling solvents, and urea, phthalic anhydride, and chloroauric acid were fused, but in all cases either phthalocyanine and gold were recovered or nothing resembling a phthalocyanine was formed. Consequently, at the temperatures usually required for the formation of phthalocyanines, gold phthalocyanine cannot be extremely stable.

E. Bivalent gold

Since gold phthalocyanine could not be prepared, the water soluble complexes of gold with ethylenediamine and o-phenanthroline were tested for polarographic study. As expected, these compounds were reduced by mercury when the dropping mercury electrode was used; so a rotating gold electrode was tried. The reduction waves for the complexes and oxygen dissolved in the water came at about the same potential, preventing further study of the reduction waves for the complexes. The polarographic results showed that gold was tervalent in the two ethylenediamine complexes.

F. Miscellaneous

The titration of aqueous solutions of $[Cu(en)_2]Br_2$, $[Pd(en)_2]Br_2$, and $[Ag(en)]NO_3$ with sodium hydroxide gave no evidence for the loss of hydrogen ions by ethylenediamine. Diethylenetriamine, triethylenetetramine, and ethylenediaminetetracetic acid all reduced gold(III) compounds to metallic gold before any complexes could be isolated.

BIBLIOGRAPHY

1. Burada, A., Ann. sci. univ. Jassy, 20, 71-4 (1935).

2. Byrne, G. T., Linstead, R. P., and Lowe, A. R., J. Chem. Soc., 1934, 1019.

3. Gibson, C. S., and Colles, W. M., *ibid.*, 1931, 2407-16.

4. Hein, F., and Regler, H., Ber., 69*B*, 1692-1702 (1936).

5. Nakatsuka, Y., Bull. Chem. Soc. Jap., 11, 45-8 (1936).

6. Noyes, W. A., and Porter, P. K., "Organic Synthesis", Collective Volume I, John Wiley and Sons, Inc., New York, 1941, pp. 457-8.

7. Soc. pour l'ind. chim. a Bale, French Patent 844,567, July, 27, 1939 from Chem. Abstr., 34, 7299[2] (1940).

VITA

The author was born in Saginaw, Michigan on September 3, 1923. His elementary and secondary education was aquired in the public schools of Michigan and Tennessee. In the fall of 1940 he enrolled at Harvard with the aid of a National Scholarship, which he retained throughout his undergraduate work. The degree, Bachelor of Science in Chemistry, was awarded to him cum laude in March, 1944. Thereupon, he simultaneously began to work as a junior chemist with Tennessee Eastman Corporation on the Manhattan Project in Oak Ridge and to take night courses at the University of Tennessee. In the fall of 1944 he transferred to the University of Tennessee as a graduate assistant and devoted full time to academic work. A year later he was awarded the degree Master of Science in Chemistry. He next matriculated at Purdue University in November, 1945, to study for his doctorate, holding first a graduate assistantship and then a Purdue Research Foundation fellowship. At the end of the summer of 1947 he left Purdue to continue his studies at the University of Ilinois. He held a graduate assistantship in the Inorganic Division for the academic year 1947-8 and has been a Graduate Fellow for the fall semester of the academic year 1948-9 while at the University of Illinois.

The author is a member of the American Chemical Society, the American Association for the Advancement of Science, Sigma Xi, Phi Lambda Upsilon, and Alpha Chi Sigma.

He is coauthor of the following papers.

1. Buehler, C. A., Harris, J. O., Shacklett, C., and Block, B. P.; The Action of Formaldehyde on *m*-hydroxybenxoic acid. II. J. Am. Chem. Soc., 68, 574-7 (1946).

2. Buehler, C. A., and Block, B. P., 3-Trichloromethyl-6-hydroxy-7-chlorophthalide and its acetyl derivative. J. Am. Chem. Soc., 68, 532 (1946).

Digitized by the Internet Archive
in 2026

https://archive.org/details/IA41549807_0106